Cement and Concrete Research 107 (2018) 317–336

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Unveiling micro-chemo-mechanical properties of C–(A)–S–H and other phases in blended-cement pastes

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ARTICLE INFO

Keywords:
Microstructure
Micromechanics
Nanoindentation
Quantitative EDS
Supplementary cementitious materials
Glass powder
Metakaolin

ABSTRACT

Current demand for novel highly sustainable concrete urges improving the links between chemical and mechanical effects of supplementary cementitious materials (SCMs) on the microstructure of blended-cement pastes. In this work, coupled NanoIndentation and Quantitative Energy Dispersion Spectroscopy (NI-QEDS) was applied to disclose chemo-mechanical properties of microstructure phases in systems incorporating typical dosages of fly ash, slag, metakaolin, or glass powder. For a fixed water-to-binder ratio of 0.4, the C–(A)–S–H chemistry was significantly affected by the SCMs, while its average mechanical properties varied within the limited ranges $M \approx 25$–27 GPa, $H \approx 0.7$–0.8 GPa and $C \approx 180$–230 GPa. The SCMs further changed the arrangement of anhydrous phases and minor hydrates embedded in the C–(A)–S–H matrix, which were also characterized (e.g., Portlandite, AFm such as carboaluminates, or an hydrotalcite-like phase). Finally, engineering properties of blended-cement matrices requires tailoring both the intermix of hydrates and the rigid anhydrous SCM inclusions.

1. Introduction

Cement pastes incorporating conventional SCMs (silica fume, fly ash and slag) have been widely investigated using different modelling approaches and experimental methods (e.g., X-ray diffraction, thermogravimetric analyses, scanning-electron microscopy, calorimetry, mercury intrusion porosimetry, pore solution characterization, etc.) to assess the contents of the hydrous and anhydrous phases, the kinetics of the reaction processes, the effects of SCMs on porosity and on the liquid phase, etc. [1–4]. As an example, thermodynamics calculations showed that the expected phases in mature hydrated pastes with conventional SCMs should include not only anhydrous SCMs and C–(A)–S–H (i.e., calcium-silicate-hydrate incorporating aluminum or not), but also significant amounts of ettringite, monocarboaluminate, and possibly hydrotalcite-like phases (with Portlandite if not completely consumed) [2,5].

In addition to the commonly employed conventional SCMs, alternative SCMs such as metakaolin (MK) and glass powder (GP) have unexploited potential. On the one hand, MK produced by controlled calcination of kaolinite clay represents a highly reactive aluminum-rich cementitious material with positive influences on strength, shrinkage and durability of cement pastes, notably with respect to the resistance to the alkali-silica reaction and aggressive solutions, as well as with the immobilization of hazardous wastes [6–9]. On the other hand, GP produced by micronization of post-consumption recycled glass represents an added value product for low-grade mixed colour glass bottle fragments (i.e., soda-lime glass) [10–13]. Moreover, the pozzolanic reactivity of finely ground GP with a fineness above about 30 m^2/kg densifies the cement paste and decreases its pore connectivity, resulting in significant reduction of chloride penetrability [14–16] and higher resistance to the alkali-silica reaction [10,17,18].

As for micromechanical properties, blended-cement pastes incorporating conventional SCMs have been largely investigated by means of statistical nanoindentation [19–30], with an emphasis on the properties of low-density and high-density calcium-silicate-hydrates (LD and HD C–S–H), Portlandite (CH) and anhydrous phases. These published results generally showed that an incorporation of ~10% silica fume, ~30% fly ash or ~50% slag would not significantly affect the mechanical properties of the LD and HD C–S–H phases themselves, although the relative fraction of the latter would generally be increased [23,24,26–28]. Another study presented contrasting results showing C–S–H phases with lower mechanical properties in systems with 50% slag compared to reference cement-only systems [20]. Interestingly, the presence of other hydrated phases (e.g. monocarboaluminates or hydrotalcite-like phases) was not considered in the micromechanical analysis until the development of an advanced technique coupling

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https://doi.org/10.1016/j.cemconres.2018.02.010
Received 26 September 2017; Received in revised form 2 February 2018; Accepted 8 February 2018
Available online 20 March 2018
0008-8846/

NanoIndentation and Quantitative Energy-Dispersive Spectroscopy (NI-QEDS) [31]. This work showed that C–(A)–S–H with similar mechanical properties could be obtained in a Portland-cement-only system and in systems with cement substituted by 30% fly ash or 50% slag, although the latter system would also include a slag inner product having higher mechanical properties and embedding a hydrotalcite-like phase [31].

As for the chemo-mechanical properties of the C–(A)–S–H, atomistic modelling [32,33] and experimental investigations on pure phases [34] suggested an increased stiffness and hardness for the C–S–H unit block (of size around 5 nm [35]) with the decrease of the *Ca/Si* ratio (associated to the increase of the silicate chain length). However, electrostatic effects of the *Ca* and *Si* ions at a greater scale in the gel pores were found to have more complex consequences [36], perhaps supporting opposite observations [37,38]. Moreover, aluminum incorporation in specific sites of the C–A–S–H may provide partial healing effects possibly leading to increased strength and durability, as shown by atomistic simulations [39]. Nevertheless, the link between the chemical structure of the C–(A)–S–H and its mechanical properties has been difficult to establish in real cement systems using nanoindentation techniques due to the complex intermix of phases in the cement paste at the micrometer scale [40–46].

By applying the latest technique coupling NanoIndentation and *Quantitative* Energy Dispersion Spectroscopy (NI-QEDS) with both statistical and deterministic approaches, the objective of this investigation is to shed light on the effects of SCMs on chemo-mechanical properties of the microstructure phases and their arrangement in cement pastes. More specifically, the work demonstrates that the effects of SCMs in conventional applications are greater on the overall arrangement of the different microstructure phases than they are on the mechanical properties of C–(A)–S–H phases. The characterization of hydrous and anhydrous phases in binary blended-cement pastes incorporating SCMs in typical dosages (i.e., 30% fly ash, 50% slag, 12% metakaolin, or 20% glass powder) showed that C–(A)–S–H with different chemistry may have relatively similar mechanical properties, while the type, properties and morphological distribution of the other phases change significantly (e.g., hard unreacted SCM inclusions, AFm types, presence of an hydrotalcite-like phase, etc.).

2. Materials and methods

2.1. Cementitious materials and specimen preparation

The cement pastes investigated in this study were produced using cementitious materials commercially available in Canada. Table 1 regroup the physico-chemical properties of these materials, as measured using an Axios Advanced X-ray fluorescence spectrometer by PANalytical, a Mastersizer 2000 laser granulometer by Malvern, a Multi Pycnometer by Quantachrome and a Slimatic Blaine fineness measuring device by Intechlab.

Five binary blended-cement pastes were prepared by partial substitution of Portland cement with SCMs at dosages generally considered to provide good results: the system OPC with 100% Portland cement, the system 30FA with 30% fly ash (and 70% Portland cement), the system 50S with 50% slag, the system 12MK with 12% metakaolin, and the system 20GP with 20% glass powder. A fixed water-to-binder ratio of 0.40 was employed for all systems, which were mixed using a high-shear mixer and cast in bar molds of 25 mm × 25 mm × 285 mm. After demoulding at 24 h, the samples were cured for one year in lime water.

For each system, a specimen of about 15 mm diameter by about 3 mm thickness was cut using a slow speed saw and mounted on a metallic disk for polishing. The relatively high density of the cement matrices allowed high-quality polishing without prior embedding in epoxy (which was preferred to avoid interference of the epoxy when measuring mechanical properties). A *Struers* automatic polishing machine was employed with *Anamet* perforated cloths. The specimens were first levelled using a 15 µm diamond compound, before 10–15 min of polishing with a 6 µm oil-based diamond suspension followed by two rounds of 10–15 min of fine polishing with a 1 µm oil-based diamond suspension. Isopropanol cleaning for 3 min in an ultrasonic bath was performed between each step to ensure removal of grinding media and debris from the polishing. This method was found adequate to provide high-quality surfaces for NI-QEDS analyses, as performed in previous studies [31,38,46].

Table 1
Chemical and physical properties of raw materials, as measured by X-ray fluorescence, laser granulometry, pycnometry and Blaine tests.

Property	Portland cement (Type GU)	Fly Ash Class F (FA)	Granulated blast-furnace slag (S)	Metakaolin (MK)	Glass powder (GP)
SiO_2 (wt%)	19.7	46.5	35.4	61.1	71.5
Al_2O_3 (wt%)	4.4	23.2	10.5	28.8	1.9
Fe_2O_3 (wt%)	2.7	16.5	0.4	1.2	0.3
CaO (wt%)	61.3	4.5	42.0	3.5	10.6
MgO (wt%)	2.9	1.0	7.9	0.5	0.8
SO_3 (wt%)	4.0	0.7	1.8	0.2	0.1
Na_2O (wt%)	0.3	0.8	0.2	0.1	12.8
K_2O (wt%)	0.9	1.9	0.3	1.7	0.6
TiO_2 (wt%)	0.2	1.1	0.5	0.6	0.1
Loss on ignition (wt%)	2.7	2.7	0.3	1.8	1.0
Si/Ca (at.)	–	9.58	0.78	16.2	6.27
(Fe + Al)/Ca (at.)	–	8.20	0.28	9.22	0.21
Mg/Ca (at.)	–	0.30	0.26	0.21	0.11
D_{10} (µm)	3.8	1.9	1.6	1.5	6.0
D_{50} (µm)	15.3	12.9	10.3	6.5	13.1
D_{90} (µm)	49.3	57.5	32.3	25.1	28.3
Density (g/cm^3)	3.11	2.54	2.89	2.58	2.52
Blaine fineness (m^2/kg)	445	382	607	1763	615

2.2. Nanoindentation measurements

The samples were kept under slight vacuum and tested shortly after polishing by nanoindentation using an Anton-Paar Ultra-Nanoindentation Tester (UNHT) installed in a cleanroom with a controlled relative humidity of 30 ± 3% and a controlled temperature of 20 ± 1 °C. Following a protocol described in detail elsewhere [46], force-controlled trapezoidal loadings were performed with a loading rate of 30 mN/min up to a penetration depth of h_{max} = 250 nm where the force was maintained for 60 s before an unloading phase at 30 mN/min. The indentation Modulus (*M*), the indentation Hardness (*H*) and the contact Creep modulus (*C*) were calculated from the load-penetration curves using previous definitions of the parameters [47–49], the Oliver and Pharr method [50,51] and a calibration of the tip on a standardized fused silica sample.

For each system, a grid of 30 × 21 indentation points spaced by 10 µm was performed to investigate a Region of Interest (ROI) representative of the heterogeneous microstructure. Abnormal load-penetration curves related to surface defects such as pores, cracks or uneven regions were removed following visual inspection. The exact location of each indent on the surface was identified from 50× stitched optical micrographs of the ROI using an indent locator script previously developed [46].

2.3. SEM-EDS quantitative measurements and qualitative mapping

After nanoindentation measurements, the specimens were stored in isopropanol for several weeks to remove the free water (and to avoid further hydration or carbonation) before the analyses in the Scanning Electron Microscope (SEM). To avoid charging during high-vacuum SEM analyses, the samples were then coated with about 15 nm of carbon (after 24 h of vacuum drying). A Hitachi S-3400 N SEM equipped with an Oxford Inca Energy 250 Energy-Dispersive